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16. ABSTRACT

Perchloroethylene (PCE), a solvent used in dry cleaning, has been suspected of contributing significantly to photochemical ozone/oxidant (O_3/O_x) problems in urban atmospheres. Past evidence, however, was neither complete nor consistent. To interpret more conclusively the past evidence, and further understand PCE's role in the O_3/O_x problem, a smog chamber testing program was conducted. The program's objectives were: (a) to explain the mechanism of the PCE reaction in smog chamber atmospheres, and (b) to extrapolate the smog chamber findings regarding PCE reactivity to the real atmosphere. Results showed that (a) in smog chambers, PCE reacts and forms O_3/O_x following a Cl-instigated photooxidation mechanisms rather than the OH-initiated mechanism accepted in current smog chemistry, and (b) in the real atmosphere neither the Cl-instigated nor the OH-instigated photooxidations of PCE can generate substantial concentrations of O_3/O_x. In fact, PCE contributes less to the ambient O_3/O_x problem than equal concentrations of ethane.

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Photochemical Reactivity of Perchloroethylene: A New Appraisal

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Perchloroethylene (PCE), a solvent used in dry cleaning, has been suspected of contributing significantly to photochemical ozone/oxidant (O_3/O_x) problems in urban atmospheres. Past evidence, however, was neither complete nor consistent. To interpret more conclusively the past evidence, and further understand PCE's role in the O_3/O_x problem, a smog chamber testing program was conducted. The program's objectives were: (a) to explain the mechanism of the PCE reaction in smog chamber atmospheres, and (b) to extrapolate the smog chamber findings regarding PCE reactivity to the real atmosphere. Results showed that in smog chambers, PCE reacts and forms O_3/O_x following what appears to be a Cl instigated photooxidation mechanism rather than the OH initiated mechanism accepted in current smog chemistry. The evidence, collectively, strongly supported this conclusion even though the source of Cl atoms could not be identified with confidence. It was further concluded that in the real atmosphere neither the Cl instigated nor the OH instigated photooxidations of PCE can generate substantial concentrations of O_3/O_x. In fact, PCE contributes less to the ambient O_3/O_x problem than equal concentrations of ethane.

The approach adopted by EPA to reducing photochemical ozone (O_3) and other oxidants (O_x) has been based on unilateral control of the volatile organic compound (VOC) precursors. However, since the individual VOC differ widely in O_3 or O_x forming potential, EPA accepted the concept of discriminate control of organic emissions, and produced from time to time lists of VOC that could be exempted from O_3 related control by virtue of their negligibly low photochemical reactivity.

Perchloroethylene (PCE), a VOC used as a solvent and emitted in significant amounts from dry cleaning operations, was first thought to be unreactive and was exempted from control. Thus, based on some Los Angeles Air Pollution Control District (LAAPCD) studies in the 1960's,[1] PCE was included among the unreactive VOC listed in EPA's "Appendix B" rule[2] and in the Los Angeles Rule 66.[3]

In the years following the LAAPCD studies, there were several other PCE reactivity studies, based on which EPA judged that PCE's reactivity is not sufficiently low to justify total exemption from O_3 related control.[4-6] More recently, there have been additional studies reported, some directly addressed to PCE's O_3 forming reactivity[7-10] and some to various mechanisms of PCE photooxidation.[11] The new evidence appeared to be partly in agreement and partly in disagreement with the latest EPA judgment. However, it became also apparent that most of the conflicting evidence could be reconciled. This led to reexamination of the question of PCE reactivity in the light of the reconciled evidence; it was concluded that more experimental testing was needed to reconcile conflicting data and to provide a scientifically more credible basis of judging the reactivity of PCE.

The Concept of Reactivity

Definitions, significance, and applications of the VOC reactivity concept in air pollution problems have been discussed in detail elsewhere.[12] The reactivity aspect of interest in this report is the ability of the VOC to participate in atmospheric reactions and form O_3/O_x. The prevalent method for measuring such reactivity has been the smog chamber method: the test VOC is exposed in a smog chamber to reactant mixture and radiation conditions similar to those in real urban atmospheres, and the yield in O_3/O_x is measured directly.

In the past nearly three decades there have been numerous smog chamber studies of VOC reactivity, and O_3/O_x yield reactivity data are now available for a large number of VOC.[12] There are problems, however, in using the existing data base for this particular reactivity index. One problem is that the O_3/O_x reactivity is not a single-value molecular property. The smog chamber method of measurement does not give a single result; it gives results that vary depending, for example, on the reactant concentration conditions used in the chamber. Thus, the O_3/O_x yield reactivities of VOC are not uniquely defined, absolutely or relative to each other, and this confuses the application of the reactivity concept in control. Another problem is that the O_3/O_x yield reactivity cannot be used for VOC of small but significant reactivity, because smog chambers manifest levels of background reactivity comparable to those of such VOC.

These problems with the O_3/O_x yield have had two consequences. They forced researchers and regulators (a) to turn to simple, two-class reactivity classification schemes (reactive, unreactive) in preference to individual VOC reactivity ranking schemes, and (b) to consider other less direct but more usable reactivity indices. The reactivity indices considered and used here are the "O_3/O_x yield" reactivity and the "VOC consumption rate" reactivity. The O_3/O_x yield reactivity data are

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Table I. Experimental systems used and results from PCE reactivity studies.

Study reference	Chamber and radiation system design	Reactant concentrations, ppm (v/v) for organic, ppm for NO_x	Avg. rate of PCE reactions %/h	Max. O_3/O_x conc., ppm	Comments
Schuck and Doyle (1959)[13]	520-ft³ glass-lined chamber with 24 400-watt H-1 mercury arcs and 78 blacklight lamps inside the chamber. Light intensity in near-UV approximately equal to full sunlight.	PCE/NO_x: 3/1	5.4	0.05	PCE rate was comparable to those for C_7-C_8 paraffins. O_3/O_3 yields for methane and trichloroethylene were 0.
Brummelle *et al.* (1966)[1]	1180-ft³ aluminum-glass chamber, with 12 GE H-400-E mercury vapor lamps and stainless steel reflectors, positioned outside the chamber behind Pyrex glass panes, and 48 GE-F-40-T-12-BL blacklight lamps placed inside the chamber. Radiation intensity approximately equal to full noonday sunlight in Los Angeles. Chamber temperature close to 100°F	PCE/NO_x: 6.34/1.85	6.4 (estimated from total organic measurements by IR)	0	Inadvertent chamber dilution was 6.3%/h. Background O_3/O_x formation as high as 0.21 ppm with 0.75 ppm background NO_x concentration.
Wilson (1971)[7]	268-ft³ aluminum-Pyrex glass chamber with all inside surfaces Teflon-coated. 72 F72T12/D/VHO daylight, 30 F40B bluelight, 28 F40BL blacklight, and 50 F40 sunlamps were used external to the chamber. Radiation intensity was 60% to 80% of noonday sunlight in Los Angeles. Chamber was operated at ~95°F.	PCE/NO_x: 8/1	4	0.11	Inadvertent chamber dilution was 3–4%/h.
		: 8/1	5	0.08	
Kopczynski (1971)[15]	335-ft³ aluminum chamber with Tedlar windows, and with 24 sunlamps, 36 blue lamps and 88 blacklight lamps positioned externally to the chamber. Radiation intensity was equivalent to k_D = 0.4 min. Chamber was operated at 90°F.	PCE/NO_x: 2/1	5–6	0	
Lillian *et al.* (1975),[6] and Appleby (1976)[17]	200-lit Teflon bag irradiated with 12 GE F40 BLB, 6 GE F40 BL and 6 Westinghouse FS40 sunlamps. Radiation intensity equivalent to k_D = 0.39 min^{-1}. Chamber was operated at 95°F.	PCE/NO_x: 0.85/0.5	4.0 during first 2 h and 12.5 over entire 8-h run	0.50	Radiation in the 2800–3000Å range was about 10 times that of natural sunlight.
		PCE/NO_x: 0.8/0	6.2 during first 2 h and 25.0 over entire 4-h run	0.01	All runs showed an induction period of 1–4 h.
Gay *et al.* (1976)[10]	690-lit borosilicate glass chamber serving as absorption cell of FTIR spectrophotometer. 96 GE F40 BLB blacklight lamps external to chamber. Radiation intensity equivalent k_D = 0.66 min^{-1}. Chamber was operated at 86°F.	PCE/NO_x: 5/1.8	2.3–7	0.07	The chamber is the same as the one used in present study but with different radiation system.

more reliable for reactive VOC and are used to classify those organics. The classification of low-reactivity VOC, for which the smog chamber measurements of O_3/O_x yield are generally unreliable, is based mainly on VOC consumption rate reactivity data, explained below.

The VOC consumption rate is the rate at which the VOC reacts under atmospheric conditions, and can be measured during the same smog chamber test used to measure the O_3/O_x yield reactivity. Its significance lies mainly in the fact that a VOC cannot produce O_3/O_x unless it participates—and, hence, is consumed—in the atmospheric reaction. The VOC consumption rate, therefore, offers the most reliable basis for recognizing the totally unreactive VOC. Thus, VOC whose consumption rates are negligibly small are classified as unreactive. By extension, it was also assumed, at first, that VOC manifesting significant consumption rates in smog chambers

Study reference	Chamber and radiation system design	Reactant concentrations, ppm (v/v) for organic, ppm for NO_x	Avg. rate of PCE reactions %/h	Max. O_3/O_x conc., ppm	Comments
Dilling *et al.* (1976)[8] and Dilling *et al.* (1976)[9]	9.6-lit Pyrex glass chamber irradiated with 2 GE 275-W reflector sunlamps with wavelength cutoff of 2900Å. Radiation intensity equivalent to ~2.6 times that of sunlight on summer day in Freeport. TX. Chamber was operated at 81°F.	PCE/NO_x: 50/12 : 10/5 : 40/20 : 100/50	~20 4–6 ~7 ~13	0 No data No data No data	
Dimitriades and Joshi (1977)[5]	400-lit Teflon-Pyrex chamber irradiated with 22 GE-F40 BLB blacklight and 7 Westinghouse SF-40 sunlamps. Radiation intensity was equivalent to k_D = 0.34 min^{-1}. Chamber was operated at 86°F.	PCE/NO_x: 4/0.2 (9 tests)	5–45 during first 1 h and 20–55 over entire run	0.5–1.2	There was an induction period of 0.5–1 h.
Yanagihara *et al.* (1977)[19] and Japan Environmental Agency (1975)[20]	70-ft^3 Pyrex chamber irradiated externally with 96 lamps including FL40A, FLR40SBL-A and FLR40SE-A types with output energy peaks at 4,200Å, 3,650Å, and 3,100Å, respectively. Radiation intensity equivalent to k_D = 0.33 min^{-1}. Chamber was operated at 86°F.	PCE/NO_x: 2/1	No data	0	
Gay (1977)[21]	690-lit borosilicate glass chamber used and described here by these authors. Irradiated by 72 BLB 40 blacklight and 24 FS40 sunlamps. Radiation intensity equivalent to k_D = 0.66 min^{-1}. Chamber operated at 86°F.	PCE/NO_x: 4/0.2	5–8	0.4	
Sickles *et al.* (1980)[23]	Four 1000-ft^3 Teflon chambers and several 250-lit Teflon bags, irradiated by natural sunlight in September–November at Research Triangle Park, NC.	PCE/NO_x: 4/0.2	Low but significantly greater than zero	0.4–0.5	Irradiation of purified air resulted in 0.06–0.07 ppm O_3. Irradiation of ambient air resulted in 0.23–0.29 ppm O_3. Irradiation of ambient air with 0.07 ppm NO_x resulted in 0.01–0.06 ppm O_3.
Kaiserman and Corse (1981)[22]	400-ft^3 aluminum chamber with Teflon windows, irradiated by 112 GE F96T8-BL blacklight and 18 Westinghouse FS20 sunlamps. Radiation intensity equivalent to k_D = 0.4 min^{-1}. Chamber operated at 90–104°F (rising T during irradiation test).	PCE/NO_x: 4/0.2	9.5	0.4	

are reactive. This latter assumption, however, has been questioned by some recent studies,[5] and as discussed later, by this study also.

Analysis and Interpretation of Existing Evidence on PCE Reactivity

Existing evidence considered here consists mainly of data on the O_3/O_x yield and PCE consumption rate reactivities obtained in the laboratory. Since crude measures of consumption rate reactivity can also be derived from ambient concentration and emission rate data, these will also be included in this analysis. Each piece of reactivity data is critiqued to the extent allowed by the reported information, and labeled as supporting a "negligibly reactive" or "reactive" classification for PCE. Negligibly reactive is defined here as equal or less reactive than ethane, the latter organic taken by the authors to be a boundary species separating the reactive VOC from the unreactive ones.

Laboratory Data on O_3/O_x Yield and Consumption Rate Reactivities

Reports on O_3/O_x yield and consumption rate reactivities of PCE, including some specifics on smog chamber system and conditions used, are listed in Table I.

The Schuck and Doyle data[13] support negligible O_3/O_x-

yield reactivity and appreciable consumption rate reactivity for PCE but are suspect because they show trichloroethylene to be less reactive than PCE, a result that is inconsistent with all other studies of the two chloroethylenes. The Brummelle, *et al.*, data[1] also support negligible O_3/O_x yield reactivity and appreciable consumption rate reactivity for PCE, but they are also suspect because of excessively high chamber background reactivity problems, and because of poor analytical methods. The Wilson data[7,14] suggest borderline levels of O_3/O_x yield and consumption rate reactivities, but they may be somewhat low because the chamber's radiation in the 3000–4000Å wavelength region—which is the most energetic part of the surface sunlight spectrum—was, according to the investigators, some 15% less than the estimated natural radiation in Los Angeles.[14] The Kopczynski data[15] support negligible O_3/O_x yield reactivity for PCE, but because of their limited amount, are questionable. The Lillian, *et al.*[6] and Appleby[16] studies resulted in high O_3/O_x yields and PCE consumption rates which, however, strongly disagreed with the previous studies. The early data by Gay, *et al.*[10] support a negligible O_3/O_x yield reactivity and a possibly significant consumption rate reactivity, but are suspect because they are limited in amount. The Dilling, *et al.* data[8,9] support negligible O_3/O_x yield reactivity and significant consumption rate reactivity but, because the apparatus and conditions used in that study are drastically different from the other studies and highly unrealistic, they cannot be quantitatively compared with the other studies and do not have absolute validity. The Dimitriades and Joshi data[5] support a reactive nature for PCE with respect to both O_3/O_x yield and consumption rate, but are suspect because of apparent inconsistencies with current smog chemistry. Thus, the reactivites of some organics that have been studied in that chamber, including methane and propane, were greater than those estimated on the basis of current smog chemistry.[17,18] The Yanagihara, *et al.* studies[19,20] resulted in O_3 yields that were comparable to background O_3 reactivity, supporting, therefore, negligible reactivity for PCE. Later studies by Gay[21] and Kaiserman and Corse[22] using two smog chambers resulted in data supporting high PCE reactivity with respect to both O_3/O_x yield and consumption rate. Finally, the Sickles, *et al.* study[23] resulted in data that support high reactivity with respect to O_3/O_x yield and a consumption rate reactivity that is comparable to or greater than that of ethane.

Atmospheric Data on Consumption Rate Reactivity

A semi-quantitative estimate of PCE reactivity can be derived from atmospheric data as follows:[24–26] The 1977 PCE emissions of 0.57×10^6 metric tons, assumed to be discharged all in the northern hemisphere, are calculated to create an ambient concentration of 40 ppt. The observed northern hemisphere concentration in well mixed air masses is 40 ppt, indicating an extremely low PCE consumption rate. Assuming the ambient PCE concentration to be constant (a reasonable assumption[24–26]), it follows that the annually added PCE concentration of 40 ppt is offset by atmospheric consumption the rate of which, obviously, is 100% per year or 0.02% per daylight hour. For comparison, the ethane removal rate, calculated from the ethane + OH rate constant $k_{OH} = 0.3 \times 10^{-12}$ cm^3 molecule sec^{-1}, and the seasonally averaged tropospheric OH concentration of 3 to 4×10^5 molecules/cm^3,[26] is 0.03 to 0.04%/h. Thus, the atmospheric data appear to support an extremely low PCE reactivity, comparable to and perhaps lower than that of ethane.

Table II. Reported laboratory studies and results on PCE reactivity.

Investigators	PCE Reactivity Found: O_3/O_x yield	PCE Reactivity Found: Consumption rate	Comments
Shuck and Doyle[13]	Negligible	High	Results are suspect because of inconsistency with other, reliable evidence.
Brummelle *et al.*[1]	Negligible	High	Results are suspect because of excessive chamber background reactivity and poor analytical methods.
Wilson[7]	Borderline	Borderline	Uncertainties exist due to unrealistic radiation conditions.
Kopczynski[15]	Negligible	High	Uncertainties exist due to limited number of experiments.
Lillian *et al.*[6,16]	High	High	Questions raised by high results relative to other studies.
Gay *et al.*[10]	Negligible	High	Uncertainties exist due to limited number of experiments.
Dilling *et al.*[8,9]	Negligible	High	Reactant concentration and radiation conditions were considerably unrealistic.
Dimitriades and Joshi[5]	High	Very High	Some results are inconsistent with current smog chemistry.
Yanagihara *et al.*[19]	Negligible	No data	
Gay[21]	High	High	
Kaiserman and Corse[22]	High	High	
Sickles *et al.*[23]	High	Borderline	Data quality could not be checked since explicit consumption rate data were not reported.

Analysis and Interpretation of Existing PCE Reactivity Data

Table II summarizes the existing laboratory and aerometric data from the 12 studies cited here. Six supported high or borderline O_3/O_x yield reactivity, six supported negligible O_3/O_x yield reactivity, and all of the studies supported high but widely varying consumption rate reactivities. The aerometric data supported negligible reactivity. Such a high level of inconsistency in experimental reactivity measurements is unusual but not surprising in the case of PCE. The Rutgers University researchers also observed highly irreproducible results in repeated irradiations of PCE/NO_x systems.[16] The same phenomenon was also observed by Dusoleil, *et al.* in their studies of the kinetics of PCE photochlorination.[27]

In searching for clues to the causes of these inconsistencies, the smog chamber studies' results were compared with reactivities deduced from smog chemistry considerations. To explain, currently accepted smog chemistry (derived from atmospheric chemistry studies of hydrocarbons and aldehydes) explains VOC reactivity in terms of the VOC's ability to participate in a chemical process, a key step of which invariably is the initial reaction of the VOC with OH radicals.[12] Reactions subsequent to the OH attack also have a role in the overall O_3

forming process, but, obviously, only if the initial reaction with OH occurs at a significant rate. Therefore, the value of the rate constant for the PCE + OH reaction, k_{OH}, can provide a useful first check on the reliability of the existing laboratory data, as explained next.

Using a k_{OH} value of 0.2×10^{-12} cm^3 molecule^{-1} sec^{-1},[28] and assuming that ambient OH concentration during summer noon time in the southern U.S. is 5×10^6 molecules cm^{-3} (reported values range within 2 to 8×10^6),[29] the PCE consumption rate in ambient air due to reaction with OH is calculated to be

$$\frac{\Delta[PCE]}{[PCE]\Delta t} \times 100 = k_{OH}[OH] \times 100 = 0.2 \times 10^{-12} \times 5 \times 10^6 \times 100 = 10^{-4}\%/\text{sec} = 0.36\%/\text{h}. \quad (1)$$

Since the light intensities in all smog chambers studied cited here except Dilling, *et al.*[8,9] are comparable to natural sunlight intensity, according to theory, the PCE consumption rates in the chambers should be roughly close to 0.36%/h. The actual observed consumption rates, however, are 1–1½ orders of magnitude higher, which means either that the smog chambers in the studies cited here did not perform consistently with smog chemistry predictions, or that current smog chemistry, for some reason, is not applicable in the PCE case. To further evaluate these two alternate explanations, consumption rates were computed from k_{OH} data for several VOC (hydrocarbons and halocarbons), and compared with those observed in the smog chambers. Computation results and the comparison are shown in Table III.

The Table III data show generally good agreement between observed and predicted consumption rate reactivities for hydrocarbons but extremely poor agreement for halocarbons. The halocarbon data disagreement is invariably in the direction of higher observed than computed reactivities, and seems to be highest for the PCE and lowest for the haloalkane. Therefore, the inconsistencies of the existing PCE reactivity data base cannot be attributed directly to smog chamber related factors alone. The more logical conclusion is that current smog chemistry cannot be applied to PCE, or more specifically, the reaction with OH is not the key step in the halocarbon consumption process. Some species, more potent than OH, must be responsible for the rapid PCE consumption in smog chambers. This raises four questions:

1. What are the chemical species that cause rapid PCE reaction in smog chambers?
2. What is the chemistry of the process following these species attacks? Does it result in O_3/O_x production?
3. Does this chemistry explain the inconsistencies among the various studies' data (Table II)?
4. Are these species and associated chemistry operative in the real atmosphere?

The first and second questions can be answered with reasonable certainty by referring to basic PCE chemistry studies. Based on studies on PCE reactions with such species as O_3, OH radicals, and O and Cl atoms, it has been established that the reaction with O_3 is too slow to account for the rapid PCE disappearance observed in smog chambers.[10,11,16] In contrast, PCE reacts rapidly with Cl atoms, obeying a chain mechanism.[11,30] The reactions with O atoms and OH radicals (0.8×10^{-13} cm^3 molecule^{-1} sec^{-1} and 2×10^{-13} cm^3 molecule^{-1} sec^{-1}, respectively)[11,28] have lower rate constants than the reaction with Cl (53.0×10^{-13} cm^3 molecule^{-1} sec^{-1}),[31] but they may be releasing Cl atoms that could accelerate PCE consumption through autocatalysis.

Besides the evidence from the kinetic studies, some smog chamber data also suggest that Cl atoms have a major role in the rapid PCE reaction observed in smog chambers. For example, injection of small amounts of Cl_2 in irradiated PCE/NO_x/air systems caused a temporary but pronounced acceleration of PCE consumption.[9] Also, presence of an effective Cl atom scavenger was observed to inhibit the PCE reaction.[9,16] Finally, the pattern of PCE and O_3 disappearing rapidly in parallel, displayed in the Lillian-Appleby,[6,16] Dimitriades-Joshi,[5] Sickles, *et al.*,[23] and Joshi-Bufalini[32] studies, can be explained as caused by Cl atoms chain-reacting with and consuming both PCE and O_3, the latter being as follows:[33]

$$O_3 + Cl \rightarrow O_2 + ClO \quad (2)$$

$$ClO + O_3 \rightarrow 2O_2 + Cl \quad (3)$$

All these kinetics and smog chamber studies suggest that the PCE consumption observed in smog chambers is caused by a Cl instigated chain photooxidation process, which evidently is also capable of generating O_3. Key reactions in this mechanism are the chain initiation steps resulting in Cl atoms. Whether these steps are photolyses of PCE and/or its reaction products or are reactions following attack of OH or O atoms on PCE it is not known, nor can it be speculated upon based on the studies reported to date. Also, the past studies did not investigate adequately the effects upon the generation and

Table III. Comparison of consumption rates observed in smog chambers with consumption rates computed from k_{OH} data for hydrocarbons and halocarbons.

Smog chamber data	Hydrocarbons/halocarbons consumption rate, %/h: Observed	Computed
Schuck and Doyle[13]		
Iso-octane	6	6.7
Ethylene	9	9–18[a]
Propylene	115	9–47[a]
Xylene	64	34
Trichloroethylene	17	4.1
PCE	5.4	0.4
Wilson[7]		
Trichloroethylene	~13	4.1
PCE	~5	0.4
Kopczynski[15]		
Butane	5–6	5.4
PCE	~5	0.4
Lillian *et al.*[6,16]		
PCE	~70 (max)[b]	0.4
Trichloroethylene	~20 (max)[b]	4.1
Vinyl Chloride	~18	11.9
1,1,1-Trichloroethane	~0	0.03–0.05
Gay *et al.*[10]		
Ethylene	~15	9–18[a]
Trichloroethylene	70 (max)[b]	4.1
PCE	~2.5, ~7	0.4
Dilling *et al.*[9]		
Toluene	14	7.2–10.8[a]
Trichloroethylene	~30	4.1
PCE	~40	0.4
Dilling *et al.*[8]		
Toluene	~7	7.2–10.8[a]
Ethylene	~15	9–18[a]
Cyclohexene	50–150	122
Trichloroethylene	14–17[c]	4.1
PCE	3.5–6[c]	0.4
Dimitriades and Joshi[5]		
Ethane	0.5	0.5
Propane	2	1.4–3.6
Butane	1.4	5.4
PCE	13	0.4
Gay[21]		
Butane	3.3	5.4
PCE	~4	0.4

[a] Range represents range of k_{OH} values reported. Only the reaction with OH was considered.
[b] Observed maximum rate.
[c] Range represents results for varying NO_2/NO_x ratios in initial chamber mixture.

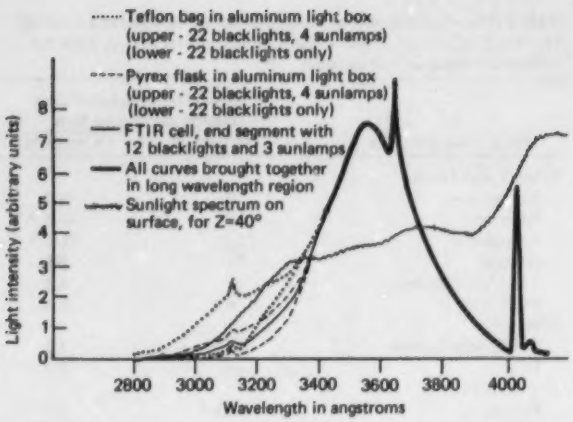

Figure 1. Near-UV spectra of radiation within various smog chambers.

fate of the Cl atoms, of those experimental factors that differed from study to study (e.g., the radiation and chamber wall related factors). In the absence of such evidence, the question whether the Cl instigated photooxidation mechanism can explain past conflicting results cannot be answered. Finally, past evidence is lacking in that it does not permit extrapolation of the laboratory data on PCE reactivity to the real atmosphere. All these deficiencies in the existing evidence led to a new study, and a reexamination of the question of PCE reactivity in the light of new experimental data.

Experimental Procedures and Results of New PCE Reactivity Study

The analysis of existing evidence on PCE reactivity indicated the following experimental objectives: (a) to confirm that in the smog chamber measurements of PCE reactivity, the operative chemistry in PCE degradation is Cl rather than OH instigated photochemistry, (b) to understand such Cl chemistry well enough to reconcile some seemingly conflicting evidence, and (c) to extrapolate the laboratory findings on PCE reactivity to the real atmosphere.

To achieve the first objective, tests were conducted in which PCE was reacted with Cl atoms, and tests in which PCE was reacted both in the presence and the absence of Cl scavengers. Also, direct photolysis of PCE and of some of its photooxidation products was explored as possible sources of the Cl atoms that instigate the rapid disappearance of PCE observed in some smog chambers. To achieve the other objectives, smog chamber irradiation tests were conducted to determine the effects on PCE consumption of the following factors: initial PCE concentration, presence/concentration of organic coreactant, radiation spectrum, chamber wall material, and chamber use before the test.

The irradiation tests used as smog chambers the absorption cell of a long path Fourier Transform Infrared Spectrophotometer (FTIR) and several bags made of Teflon. The FTIR cell and associated IR-measurement instrumentation and procedures have been described in detail elsewhere.[10] Briefly, the FTIR chamber is a 690-liter borosilicate segmented glass tube surrounded by banks of fluorescent lamps (consisting of 24 FS 40 sunlamps and 72 BLB 40 blacklight lamps). Total radiation intensity inside the FTIR chamber, measured through irradiation of NO_2-N_2 mixtures, was found to be equivalent to a first order NO_2 disappearance rate constant, k_D, equal to 0.66 min^{-1}.[34] The bag chambers were 60-L to 360-L bags made of 2-mil fluorinated ethylene-propylene (FEP) Type A Teflon film. For irradiation, one or two bags were suspended inside an 0.8 m × 1.4 m × 1.1 m aluminum box fitted with 22 BLB 40 blacklight lamps and 4 FS 40 sunlamps evenly distributed along two opposite sides. The radiation intensity inside a bag was equivalent to $k_D = 0.45$ min^{-1}. More details on the aluminum box chamber and operating procedures can be found elsewhere.[35] The near-UV spectra of the radiation inside the various smog chambers used, from the blacklight lamps alone and from all lamps are shown in Figure 1. The smog chambers were operated at either 25 ± 2°C (bags) or 30 ± 2°C (FTIR).

Measurements of PCE and of other reactants or products in the FTIR chamber were made by infrared spectrophotometry.[10] Measurements in the Teflon bag chambers were made by gas chromatography (GC) coupled with either flame ionization detection (FID) or electron capture detection (ECD). The GC system included a 6 ft × ⅛ in. O.D. stainless steel column packed with 10% SF-96 on 60/80 mesh Chromosorb W-AW, and operated at 100°C. The carrier gas was helium for the GC/FID measurements, or 5%-methane-in-argon for the GC/ECD measurements. Results from repeated measurements upon several calibration mixtures during a 2½-month period showed a precision equivalent to a coefficient of variation of 23%.[36]

The PCE reagent was of research grade quality with better than 99% purity. It was found to contain traces of 5-methylisoproponol which has a boiling point of 232.9°C. For purification, the reagent was freshly redistilled, discarding the fractions outside the 119–119.5°C boiling range. All other reagents were purchased in their purest form commercially available and were used without further purification.

A more detailed description of the apparatus and experimental procedures and the statistical evaluation of the analytical methods used can be found elsewhere.[36]

Thirty-seven smog chamber tests were conducted. Table IV shows the initial conditions used and results for the various FTIR and Teflon bag tests in chronological order. A reasonable amount of test replication was applied to ascertain the significance of the observed effects.

Evidence of the role Cl chemistry plays in PCE smog chamber tests was provided by tests 4, 5, 6, and 8, in which PCE was irradiated in the FTIR chamber in the presence and the absence of Cl_2. Results from all four tests consistently showed that the injected Cl_2 accelerated the PCE reaction by factors of 1.6–6 (Figure 2).

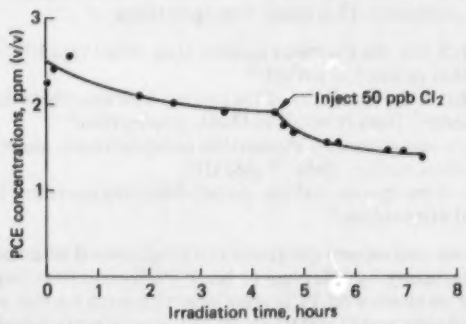

Figure 2. Effect of Cl_2 on photooxidation of PCE (FTIR chamber).

Additional evidence on the role of Cl chemistry was provided by the FTIR tests 1, 3, 4, 5, 6, 8, and 11 and Teflon bag tests 12, 13, 14, and 23–30, in which PCE was irradiated in the presence and the absence of another organic compound capable of scavenging Cl atoms. The scavenger organic compounds used were trichloroethylene (TCE) (FTIR tests) and n-butane (Teflon bag tests). Results from the FTIR tests showed that TCE, present at a concentration equal to that of PCE (and with a rate constant for the TCE + Cl reaction equal to about 11 times that of the PCE + Cl reaction)[37] inhibited the PCE reaction by approximately a factor of 2. The Teflon

Table IV. Initial conditions and results of smog chamber tests.

Test No.	Date	Test Conditions: Chamber/ Radiation	Test Conditions: Reactant mixture (in zero tank air)	Test Results: Average rate of PCE reaction %/h	Test Results: Irradiation period	Test Results: Comments
1	2/25/82	FTIR chamber All lamps on	2 ppm PCE 0.5 ppm NO_2	13.8 9.3	First h First 5 h	O_3 built up to 0.28 ppm.
2	2/25/82	FTIR chamber All lamps on	2.5 ppm trichloroethylene 0.5 ppm NO_2			Trichloroethylene disappeared at the rate of ~25%/h. O_3 built up to 0.5 ppm.
3	3/1/82	FTIR chamber All lamps on	2 ppm PCE 2 ppm trichloroethylene 0.5 ppm NO_2	4.0 3.8	First h First 5 h	Trichloroethylene disappeared at the rate of 30%/h in the first 1 h, and 24.3%/h in the first 5 h. O_3 built up to 0.21 ppm.
4	3/2/82	FTIR chamber All lamps on	9.2 ppm PCE, 0.5 ppm NO_2 } Initially Add 100 ppb Cl_2 after 4 h irradiation	10.3 4.8 64.0	First h First 4 h. First h following Cl_2 injection	O_3 built up to 0.2 ppm in first 4 h.
5	5/11/82	FTIR chamber All lamps on	2.6 ppm PCE, 0.5 ppm NO_2 } Initially Add 100 ppb Cl_2 after 2 h irradiation	8.1 8.1 21.5	First h First 2 h First h following Cl_2 injection	
6	5/18/82	FTIR chamber All lamps on	2.7 ppm PCE initially Add 10 ppb Cl_2 after 3.5 h irradiation	13.6 4.7 57.0 14.0	First h First 3.5 h First h following Cl_2 injection First 3 h following Cl_2 injection	
7	5/22/82	FTIR chamber All lamps on	2.8 ppm PCE 0.3 ppm trichloroacetyl chloride	6.4 6.2	First h First 6 h	Unusually large amounts of scatter in FTIR measurements of PCE. Trichloroacetyl chloride disappeared at the rate of ~3%/h.
8	5/26/82	FTIR chamber All lamps on	2.5 ppm PCE, 20% R.H. } Initially Add 50 ppb Cl_2 after 4.5 h irradiation	8.3 5.6 13.7 4.5	First h First 4 h First h following Cl_2 injection First 3 h following Cl_2 injection	
9	6/7/82	FTIR chamber Irradiate with all lamps on for 2 h, let stand in dark for 16 h, irradiate for 3 h, add 300 ppb Cl_2, irradiate for 3 h	1.0 ppm trichloroacetyl chloride	10.3[a] 4.1[a] 11.4[a] 14.7[a]	First 2 h of irradiation Dark period (16 h) First 3 h following dark period First 3 h following Cl_2 injection	Only product observed prior to Cl_2 injection was CO at 0.02 ppm; phosgene was not observed Traces of phosgene were observed following Cl_2 injection and irradiation.

[a] Data are for trichloroacetyl chloride reaction.

bag test results showed that n-butane, at concentrations as low as 4 times that of PCE (and with a rate constant equal to about 42 times that of the PCE reaction)[37] reduced the PCE reaction rate from about 100%/h to about 4%/h.

To determine whether direct PCE photolysis is the source of Cl atoms in smog chamber irradiated PCE/air systems, tests were conducted in which PCE was irradiated alone or in the presence of high n-butane concentrations (1000–10,000 ppm). The rationale for these tests was that in the presence of high concentrations of a radical scavenger (butane) the only cause of PCE disappearance would be direct photolysis. Results did not lead to unequivocal conclusions. Specifically, in tests 23, 24, and 25, (in which PCE was irradiated in the presence of butane) PCE disappeared at 0.4, 0.7, 0.3, 2.4, and 0.4%/h, whereas in tests 18 and 20 (in which the PCE mixtures were allowed to stand in the dark) the PCE disappearance rates were 0.4 and 0.2%/h. At the 70% probability level, the dark and irradiated rates (and their confidence intervals) are calculated to be 0.3 (±0.3)%/h and 0.84 (±1.1)%/h, respectively. This is interpreted to mean that, if PCE photolyzes, its photolysis rate cannot exceed approximately 1.9%/h.

The appearance of an induction period in tests in which the PCE reacted rapidly, suggested that a PCE reaction product may be a source of Cl atoms and thus exert an autocatalysis-type effect on the PCE reaction. To explore this possibility, FTIR tests 7 and 10 were conducted, in which PCE was irradiated before and after injecting trichloroacetyl chloride (TCAC). TCAC was selected because of evidence that it is a

Test No.	Date	Test Conditions: Chamber/ Radiation	Test Conditions: Reactant mixture (in zero tank air)	Test Results: Average rate of PCE reaction %/h	Test Results: Irradiation period	Comments
10	6/9/82	FTIR chamber All lamps on	2.1 ppm PCE 20 ppb trichloroacetyl chloride	5.0 5.0	First h First 6 h	Phosgene built up to ~0.1 ppm.
11	6/21/82	FTIR chamber All lamps off for 3.5 hours, Irradiate with all lamps for 1 hour following dark period	1.6 ppm PCE 2.9 ppm O_3 10.0 ppm CH_4 Initially Add 200 ppb Cl_2 after 3.5 h standing in dark	1.4 61.0	First 3.5 h First h of irradiation following Cl_2 injection	O_3 disappeared at the rate of ~0.5%/h during the dark period.
12	4/16/82	360-lit Teflon Bag #1 All lamps on	2.5 ppm PCE 40–60% R.H.	~110	First 0.9 h	There was an induction period of ~30 min following which PCE disappeared rapidly and completely. O_3 built up to ~2 ppb.
13	4/19/82	360-lit Teflon Bag #1 All lamps on	3 ppm PCE 40–60% R.H.	~110	First 0.9 h	Induction period of ~20 min. O_3 built up to ~2.5 ppb.
14	4/20/82	360-lit Teflon Bag #1 All lamps on	2.6 ppm PCE 92 ppm n-butane 40–60% R.H.	0.3	First 16.6 h	O_3 built up to 13 ppb.
15	4/21/82	360-lit Teflon Bag #1 All blacklights on All sunlamps off	2.6 ppm PCE 40–60% R.H.	0.4	First 15 h	O_3 built up to 17 ppb.
16	4/26–27/82	360-lit Teflon Bag #1 All blacklights on All sunlamps off	2.5 ppm PCE 40–60% R.H.	2.5	First 21 h	O_3 built up to 37 ppb.
17	4/27–28/82	360-lit Teflon Bag #1 All blacklights on All sunlamps off	2.5 ppm PCE 40–60% R.H.	6.5	First 20 h	O_3 built up to 16 ppb.
18	4/28–29/82	360-lit Teflon Bag #1 All lamps off	2.8 ppm PCE 40–60% R.H.	0.4	First 20 h	
19	4/29–5/1/82	360-lit Teflon Bag #1 280-lit Teflon Bag #2 (new unused bag). Following an 18-h dual bag irradiation test, the contents of Bag #2 were transferred to emptied Bag #1 and were reirradiated. All blacklights on All sunlamps off	Bag #1: 2.5 ppm PCE Bag #2: 2.4 ppm PCE 40–60% R.H.	~11 0.8 4.5	First 18 h in Bag #1 First 17 h in Bag #2 First 22 h following transfer of Bag #2 contents into emptied Bag #1	Induction period of 6 h in Bag #1. No induction period in Bag #2.

PCE photooxidation product,[10] and because it was considered the most likely reaction product that could be photolyzed by solar radiation. Although the reaction system in the FTIR system receives a relatively smaller amount of short wavelength radiation (2800–3300Å) than in the bag chambers (see Figure 1), the FTIR chamber walls still transmit enough of such radiation for the purposes of these tests. Similar tests were also conducted using Teflon bags (tests 36 and 37). Results showed no perceptible effect of TCAC on the PCE reaction. Also, consistent with this finding was the result of test 9, in which TCAC disappeared rather slowly (10.3%/h) when irradiated in the FTIR chamber. These tests showed that photolysis of TCAC could not be a significant source of Cl atoms in smog chamber photooxidation of PCE.

In an effort to reconcile some conflicting data on PCE reactivity, studies were included of some experimental factors that were known or suspected to have significant effects on the PCE reaction and to differ in the various investigations. Most important among these factors were judged to be: spectral distribution of radiation, chamber wall, and initial reactant concentration.

The radiation spectrum factor was studied in tests in which the radiation spectrum was varied either by changing the lamp composition or by using glass to filter out selected wavelengths. Specifically, the amount of 2800–3300Å radiation was disproportionately reduced either by shutting off the sunlamps or by placing the reactor bag inside a Pyrex flask. The effects of these modifications on the wavelength spectrum are shown in Figure 1. Results showed the PCE reaction to be extremely sensitive to radiation within the 2800–3300Å wavelength range. With all lamps on and without the glass screen, PCE reacted at rates from 110%/h (tests 12, 13, 29, 30, 34) to 20%/h (test 35). But with the sunlamps off or when the bag was placed inside the Pyrex flask the PCE reaction rate

Test No.	Date	Test Conditions: Chamber/ Radiation	Test Conditions: Reactant mixture (in zero tank air)	Test Results: Average rate of PCE reaction %/h	Test Results: Irradiation period	Comments
20	5/17–18/82	280-lit Teflon Bag #5 (new unused bag). All lamps off	0.7 ppb PCE 40–60% R.H.	~0.2	First 20 h	
21	5/18–19/82	280-lit Teflon Bag #3	Bag #3: 0.7 ppb PCE	~1.1	First 20 h in Bag #3	
		280-lit Teflon Bag #5 Dual bag irradiation with all lamps on for 20 h. Add HC in Bag #3 and continue irradiation	Bag #5: 0.6 ppb PCE 40–60% R.H. Following 20-h irradiation add 0.25 ppmC propylene and 0.75 ppmC n-butane to Bag #3 and continue irradiation	~1.3 ~0.5	First 20 hours in Bag #5 First 22 h following propylene/ butane injection in Bag #3	
22	5/20–21/82	280-lit Teflon Bag #5 All lamps on	55 ppb PCE 40–60% R.H.	~1.5	First 21 h	
23	6/8–9/82	280-lit Teflon Bag #5 All lamps on	2.6 ppm PCE 1000 ppm n-butane 40–60% R.H.	0.4	First 24 h	
24	6/9–10/82	280-lit Bag #4 280-lit Bag #5 (dual bag irradiation) All lamps on	2.6 ppm PCE 1000 ppm n-butane 40–60% R.H. } in Bag #4 2.6 ppm PCE 1000 ppm n-butane 40–60% R.H. } in Bag #5	0.7 0.3	First 16 h in Bag #4 First 16 h in Bag #5	
25	6/10–11/82	280-lit Bag #4 280-lit Bag #5 (dual bag irradiation) All lamps on	2.2 ppm PCE 10,000 ppm n-butane } in Bag #4 2.3 ppm PCE 10,000 ppm n-butane } in Bag #5 40–60% R.H.	2.4 0.4	First 17 h in Bag #4 First 17 h in Bag #5	
26	6/16–17/82	280-lit Bag #6 280-lit Bag #7 (dual bag irradiation) All lamps on	2.6 ppm PCE 10 ppm n-butane } in Bag #6 2.6 ppm PCE 10 ppm n-butane } in Bag #7 40–60% R.H.	0.4 0.5	First 20 h in Bag #6 First 20 h in Bag #7	
27	6/17–18/82	280-lit Bag #7 All lamps on	2.6 ppm PCE 1 ppm n-butane 40–60% R.H.	0.6	First 22 h in Bag #7	

was from 0.4 to 11%/h (tests 15, 16, 17, 19, 35). While a part of this effect is undoubtedly due to the total light intensity loss caused by the glass screen or by shutting off the sunlamps, this loss is obviously far too small to account for the drastic reduction in the PCE reaction rate. Based on these results, and on the differences in radiation spectrum between the FTIR chamber and the Teflon bag, it was concluded that the lower PCE rates observed in the FTIR chamber are mainly due to lower 2800–3300Å radiation intensity.

The smog chamber wall could have two distinct effects on the PCE reaction: one related to the radiation transmitted by the window material, and one related to the scavenging of radicals (especially of Cl atoms) by the inside wall surface. As discussed above, the radiation transmission was found in this study to be a strong factor, suggesting that when sunlamps are used in smog chambers, use of Teflon film as window material should cause relatively higher PCE reactivity measurement results. There is an abundance of evidence published on the radical scavenging role of walls. In fact, evidence has been reported for the specific case of Cl atom scavenging by Teflon surfaces. Specifically, NASA investigators reported that the strong inhibitive effect of Cl atoms on O_3 formation from O_2 photolysis was considerably reduced when the Teflon surface of their reactor was exposed to prolonged $CFCl_3$ photolysis.[38] The investigators attributed this effect to a reduction in the Cl scavenging ability of the Teflon walls, caused by excessive deposition of $CFCl_3$ reaction products. To explore occurrence of such an effect in this study, Teflon bag #1 was used 4 times in succession to irradiate 2.5–2.6 ppm PCE (with the blacklight lamps only) for several hours. Results showed the PCE loss rate to increase with bag usage, from 0.4–11%/h. Considering, however, that bag #1 had been used (and perhaps already been conditioned) before these 4 tests, and that some of the rate value variation is due to error, these results may or may not reflect a significant surface effect.

Of the initial reactant concentration factors in photochemical reactivity studies, those relevant here are the organic reactant concentration, the reactant NO_x concentration, and the organic to NO_x ratio. In the case of PCE, the data from this study indicated that the NO_x does not appreciably influence the PCE reaction rate. Thus, the reaction rates in the absence of NO_x (tests 6 and 8) are well within the range of values obtained in the presence of NO_x (tests 1, 4, and 5). Unlike NO_x, initial PCE concentration did affect the PCE rate, strongly. Thus, irradiation of 2.5–3 ppm PCE resulted in PCE rates of 20 to 110%/h, whereas for initial PCE concentrations of 0.6–55 ppb, the rates were 0.5 to 1.5%/h.

The final objective in this experimental effort was to obtain

Test No.	Date	Chamber/ Radiation	Test Conditions Reactant mixture (in zero tank air)	Test Results Average rate of PCE reaction %/h	Irradiation period	Comments
28	6/21–22/82	280-lit Bag #7 All lamps on	2.6 ppm PCE 1 ppm n-butane } in Bag #7 40–60% R.H.	0.4	First 18 h	
29	6/23–24/82	60-lit Bag #10 60-lit Bag #11 placed inside Pyrex flask (dual bag irradiation) All lamps on	2.6 ppm PCE in Bag #10 2.6 ppm PCE in Bag #11 40–60% R.H.	~110 4	First 1.1 h in Bag #10 First 21 h in Bag #11	Induction period of ~0.6 h in Bag #10
30	6/25/82	60-lit Bag #10 60-lit Bag #11 placed inside Pyrex flask (dual bag irradiation) All lamps on	2.3 ppm PCE in Bag #11 2.8 ppm PCE in Bag #10 40–60% R.H.	~110 10.6	First 0.9 h in Bag #10 First 5 h in Bag #11	
31	6/28/82	60-lit Bag #12 60-lit Bag #13 (dual bag irradiation outdoors)	2.5 ppm PCE in Bag #12 2.5 ppm in Bag #13 40–60% R.H.	3 3	First 4 h in Bag #12 First 4 h in Bag #13	Partly cloudy skies. Bags were placed on aluminum foil. No induction period.
32	6/29/82	100-lit Bag #12 100-lit Bag #13 (dual bag irradiation outdoors)	2.8 ppm PCE in Bag #12 2.4 ppm PCE in Bag #13 40–60% R.H.	4.7 2	First 4.5 h in Bag #12 First 4.5 h in Bag #13	Partly cloudy skies. No induction period.
33	6/30/82	100-lit Bag #12 100-lit Bag #13 (dual bag irradiation outdoors)	2.4 ppm PCE in Bag #12 2.3 ppm PCE in Bag #13 40–60% R.H.	2.9 3.5	First 5 h in Bag #12 First 5 h in Bag #13	Clear skies.
34	7/7–8/82	60-lit Bag #14 placed inside Pyrex flask 60-lit Bag #15 (dual bag irradiation All lamps on	2.6 ppm PCE in Bag #14 2.6 ppm PCE in Bag #15 40–60% R.H.	1 50	First 17 h in Bag #14 First 2 h in Bag #15	Induction period of ~1 hr in Bag #15
35	7/8–9/82	60-lit Bag #14 60-lit Bag #15 placed inside Pyrex flask (dual bag irradiation) All lamps on	2.7 ppm PCE in Bag #14 2.8 ppm PCE in Bag #15 40–60% R.H.	20 4	First 2.5 h in Bag #14 First 18 h in Bag #15	
36	8/12/82	280-lit Bag #18 280-lit Bag #19 All lamps on	50 ppb PCE in Bag #18 50 ppb PCE in Bag #19	0.5 0.5	First 23 h in Bag #18 First 23 h in Bag #19	
37	8/13/82	280-lit Bag #18 280-lit Bag #19 All lamps on	50 ppb PCE 5 ppb TCAC } in Bag #18 50 ppb PCE 5 ppb TCAC } in Bag #19	0.5 0.3	First 11 h in Bag #18 First 11 h in Bag #19	

evidence that would permit extrapolation of the laboratory data on PCE reactivity to the real atmosphere. Such evidence is on the effects on PCE reactivity of radiation intensity and spectrum, co-reactant organic compounds, and PCE concentration, and has already been described and discussed in connection with the other objectives. Additional tests, addressed to this objective, were parallel tests in which PCE-air mixtures were irradiated with the laboratory radiation system and with natural sunlight. Results from the natural sunlight irradiation tests (tests 31, 32 and 33) showed the PCE rates to be 2–5%/h. These rates are considerably lower than those observed in the artificial sunlight tests (tests 12, 13, 29, 30, and 35), and comparable to those observed when the 2800–3300Å component was reduced (i.e., tests 15, 16, 17, 29, 30, 34, and 35). This means that use of Teflon film smog chambers and of radiation with a strong near-UV component would tend to

cause unrealistically high PCE reactivity results, and that for extrapolation to the real atmosphere such results should be adjusted downward.

Discussion

The evidence obtained in this and the previous studies on the effects upon PCE reactivity of the initial reactant concentrations, Cl_2, and organic co-reactants, is consistent with a Cl instigated chain photooxidation mechanism analogous to the OH initiated mechanism accepted in current smog chemistry:

$$CCl_2 = CCl_2 + Cl \rightarrow CCl_3CCl_2 \quad (4)$$

$$CCl_3CCl_2 + O_2 \rightarrow CCl_3CCl_2O_2 \quad (5)$$

$$CCl_3CCl_2O_2 + NO \rightarrow CCl_3CCl_2O + NO_{2_{h\nu}} \hookrightarrow NO + O_{O_2} \hookrightarrow O_3 \quad (6)$$

$$CCl_3CCl_2O \rightarrow CCl_3C(O)Cl + Cl \quad (7)$$

$$\rightarrow COCl_2 + CCl_{3O_2} \hookrightarrow COCl_2 + ClO \quad (8)$$

In the absence of NO, main reaction products should be $CCl_3CCl(O)$ and $COCl_2$. In the presence of moderate concentrations of NO, O_3 also should form through photolysis of NO_2, as well as PAN-type products arising from the CCl_3CO radical through reactions similar to those in smog chemistry for hydrocarbons/aldehydes. Finally, as with all VOC/NO_x systems, excess NO should suppress production of O_3, PAN and other oxidants.

Conceivable sources of Cl atoms in the irradiated PCE/NO_x system are several, for example:

$$OH + CCl_2 = CCl_2 \rightarrow \rightarrow Cl \text{ (or } \rightarrow Cl_2 \xrightarrow{h\nu} 2Cl) \quad \text{or} \quad (9)$$

$$O(^3P) + CCl_2 = CCl_2 \rightarrow \rightarrow Cl \text{ (or } \rightarrow Cl_2 \xrightarrow{h\nu} 2Cl) \quad \text{or} \quad (10)$$

$$CCl_2 = CCl_2 \xrightarrow{h\nu} Cl + CCl_2 = CCl \quad (11)$$

Additionally, photolysis of the $CCl_3CCl(O)$ product could produce Cl atoms, which would tend to cause an autocatalysis-type acceleration of PCE consumption.

The rate constants for the PCE reactions with $O(^3P)$ and OH are, respectively, 0.8×10^{-13} cm^3 molecule^{-1} sec^{-1} and 2×10^{-13} cm^3 molecule^{-1} sec^{-1},[11,28] whereas the concentrations of $O(^3P)$ and OH in photochemical VOC/NO_x systems are roughly 10^{-8} ppm and 10^{-7} ppm, respectively.[39] These data show that the reaction of PCE with $O(^3P)$ may be relatively less important. Furthermore, Appleby found that PCE disappeared rapidly when irradiated in a Teflon bag in mixture with pure N_2.[16] This finding, if indeed valid, would suggest that neither $O(^3P)$ nor OH are necessarily the main instigators of the Cl releasing process. It is possible, however, that some atmospheric O_2 permeated the Teflon bag, in which case OH could not be ruled out as an instigator. Data from the current study rule out photolysis of $CCl_3CCl(O)$ as a source of Cl atoms, and tend to support direct photolysis of PCE as the most likely—although weak—source of Cl atoms in smog chamber irradiated PCE/air or PCE/NO_x/air systems. Consistent with this deduction is the fact that liquid PCE—and conceivably gaseous PCE also—absorbs strongly at wavelengths near 3000Å.[40] Other sources, e.g., reaction with OH, are not likely but cannot be completely ruled out either.

The next question of interest is whether Cl instigated PCE photooxidation explains the wide diversity of PCE reactivity results in the various studies.

With respect to the consumption rate reactivity, the present study and two others[5,6] resulted in the highest values, ranging from 20 to 110%/h, whereas all the other studies except Dilling, *et al.*[9] resulted in values of 2.3–9.5%/h. Factors the current study identified as having strong effects on the PCE consumption rate are the radiation intensity within the 2800–3300Å wavelength region, the presence of organic co-reactants, and the PCE concentration. Since widely diverse data were obtained for comparable PCE concentrations, and there were no organic co-reactants except the background contaminants (see Table I), the radiation factor could conceivably explain the diversity. PCE investigators have not reported complete quantitative data on this radiation factor but the little qualitative information available is usually consistent with this explanation. Thus, of the chambers reporting low consumption rate data, the ones of Brümmelle, *et al.*,[1] Wilson,[7] Kopczynski,[15] Gay, *et al.*,[10] Yanagihara, *et al.*,[19] and the FTIR chamber of the present study used as window material either glass or Tedlar film, both of which are less transparent to 2800–3300Å radiation than Teflon,[41] the window material used in the smog chambers of this and the Lillian, *et al.*[6] studies. Sickles, *et al.*,[23] who also reported low consumption rate results, used Teflon chambers but they also used natural sunlight radiation which, relative to the radiation used in the present study, was found to cause lower consumption rates. The Dimitriades/Joshi chamber,[5] associated with high consumption rate data, was made of glass but because of its relatively small volume and cylindrical shape, the 2800–3300Å radiation generated by the chamber's six sunlamps was more intense than in all the larger chambers except the FTIR chamber of this study.

Differences in 2800–3300Å radiation apparently do not explain the difference in consumption rate results observed between the Dimitriades and Joshi chamber[5] and the FTIR chamber of this study. Thus, considering these two chambers' diameters, the numbers of sunlamps used, and the fact that the chambers are made of the same material, the 2800–3300Å radiation intensity should be higher in the FTIR chamber. Yet the PCE consumption rates observed for comparable initial PCE concentrations were higher for the Dimitriades and Joshi chamber by a factor of approximately 2. The disagreement in this case may be related to chamber wall effects. Thus the pattern of PCE disappearance in the Dimitriades and Joshi chamber (rapid acceleration of the reaction following an induction period) is consistent with little or no scavenging of Cl atoms by the chamber walls. In contrast, the uniform PCE disappearance observed in the FTIR chamber and the tendency for the effect of injected Cl_2 to diminish with time (see Figure 2) are consistent with strong Cl scavenging by the chamber walls. Therefore, a difference in the walls' Cl scavenging ability (evidently due to different usage histories) most likely caused the disagreement in PCE consumption rate results between the two chambers.

Finally, no attempts were made to reconcile the reactivity data obtained by Schuck and Doyle[13] and by Dilling, *et al.*[9] with those of the other studies. The effects of the Schuck and Doyle chamber's unorthodox design (lamps were inside the chamber) and of the unrealistic radiation and reactant concentration conditions used by Dilling, *et al.* are not well enough understood to permit meaningful comparisons with the other studies.

With respect to the O_3/O_x yield reactivity, the proposed Cl photooxidation mechanism dictates that such reactivity should be influenced by the same factors that influence the consumption rate reactivity and additionally by the PCE to NO_x ratio factor. This means that of the reported studies, those which resulted in the highest consumption rate reactivity data, and those which used optimum PCE to NO_x ratio conditions in the smog chamber tests, should also have resulted in the highest O_3/O_x yield reactivity data. This is indeed the case, as the data in Tables I and IV show. Thus, the highest O_3/O_x yield reactivity data were obtained by Lillian, *et al.*,[6] Dimitriades and Joshi,[5] Sickles, *et al.*,[23] Gay,[21] and the present study. Of these, Lillian, *et al.*, Dimitriades and Joshi, and the

present study also gave high consumption rate reactivity results. Gay, Sickles, *et al.* and some tests of this study used a PCE to NO_x ratio of 20, which is much more conducive to O_3/O_x formation[23] than the ratios of 2–8 or >100 used in the other studies.

From the discussion thus far, it can be concluded that in smog chamber testing of PCE, current smog chemistry, with the OH attack as its key reaction step, is not operative; instead, a Cl instigated chain photooxidation chemistry is probably operative. Furthermore, in the light of this new evidence, the Cl instigated photooxidation mechanism seems to provide reasonable explanations of the reactivity differences observed in the various smog chambers. However, the most significant feature of this mechanism is that, relative to the OH initiated mechanism, it results in substantially higher levels of PCE reactivity. This raises the final and most important question, which is whether the Cl instigated photooxidation chemistry observed in smog chambers can also produce O_3 in the real atmosphere.

Analysis of atmospheric data indicated a negligibly reactive nature for PCE which suggests that the Cl chemistry is not effective in the real atmosphere. But such data are usually too limited to support reliable conclusions. One must rely, therefore, on existing laboratory evidence and theoretical deductions. The relevant laboratory evidence is the smog chamber data on the effects of various factors on PCE consumption in irradiated PCE/NO_x systems.

The PCE concentration factor was found in the present study to have a strong co-directional effect on PCE consumption rate. Thus the PCE consumption rates for initial PCE concentrations of 2.5–3 ppm were 20–110%/h, whereas for initial PCE concentrations of 0.6–55 ppb, the rates were 0.5–1.5%/h. That is, reducing initial PCE concentration by 2–3 orders of magnitude reduced the normalized PCE consumption rate by about 2 orders of magnitude. Extrapolation of these results to the real atmosphere, where the PCE concentration is only a few ppt, can be made only very roughly. Since the normalized PCE consumption rate is a function of PCE concentration, it follows that the order of the PCE reaction with respect to the PCE reactant must be greater than 1. Lacking detailed mechanism and complete kinetic data, the assumption is made that the kinetic rate equation is $R = k[\text{PCE}]^n$ (where $n > 1$) and the normalized rate (R', %/h) equation is:

$$R' \equiv \frac{R}{[\text{PCE}]} \times 100 = k[\text{PCE}]^{n-1} \qquad (12)$$

Using our data, k and n are estimated to be 31.6 and 1.77, respectively. From these results it follows that for the ambient hemispheric PCE concentration of 40 ppt,[26] the PCE consumption rate should be 0.01%/h. In urban atmospheres, where the PCE concentration can reach 1–7 ppb,[24] the PCE consumption rate can be as high as 1.75%/h. For comparison, the atmospheric reaction rate of ethane, based on its reaction with OH ($k_{OH} = 0.3 \times 10^{-12}$ cm^3 molecules sec^{-1}, [OH] = 3 to 5×10^5 molecules/cm^3) is 0.03–0.04%/h. Similar results are also derived from the Dilling, *et al.* data.[9] Dilling, *et al.* reported that reduction of the initial PCE concentration in their smog chamber from 100 ppm to 10 ppm caused the normalized PCE consumption rate to be reduced by a factor of 2.9, down to a half-life of 11.2 h. Using again the rate equation $R = k[\text{PCE}]^n$ (where $n > 1$), and the Dilling, *et al.* data, k and n are calculated to be 33.1 and 1.47, respectively, values that lead to a PCE consumption rate in the real atmosphere from 0.004%/h (hemispheric average) to 0.7%/h (urban maximum). The highest rates are higher than those of the ethane reaction with OH in the real atmosphere or of the PCE reaction with OH (Table III). Therefore, based on the effect of the PCE concentration factor alone, the PCE consumption rate reactivity, and by inference the O_3/O_x yield reactivity also, could be significant in the real atmosphere.

Co-reactant VOC capable of competing with PCE for Cl atoms were found in the present study and by others[9,16,42] to inhibit the PCE reaction in smog chambers extremely strongly. This finding is consistent with available kinetic data showing the rate constant for the Cl + PCE reaction (5.3×10^{-12} cm^3 molecule^{-1} sec^{-1}), to be 1–3 orders of magnitude lower than those for the reactions of Cl with non-methane hydrocarbons.[31,37] Another role of the co-reactants, also resulting in inhibition of the PCE reaction, could be to scavenge the radicals (e.g. OH) that instigate the Cl releasing process. Applying these results to the real atmosphere, where PCE is invariably accompanied by hydrocarbons at concentrations several hundred times its own, the PCE reaction with Cl should proceed at a rate 3–5 orders of magnitude lower than the rates of the non-methane hydrocarbon reactions with Cl. Since the ambient hydrocarbons are known to have lifetimes of hours or longer,[43] and their disappearance is due mainly to their reaction with OH rather than with Cl, the PCE reaction with Cl in the real atmosphere seems too slow to have any significance. Therefore, based on the effect of the co-reactant factor, the PCE reactivity in the real atmosphere should be negligible.

In conclusion, although the laboratory evidence currently available is not absolutely consistent and complete, it does permit collective interpretation of the diverse smog chamber data available and extrapolation of such data and findings to the real atmosphere. Furthermore, its limitations notwithstanding, the evidence clearly points to the conclusion that Cl instigated photooxidation of PCE cannot occur in the real atmosphere at a high enough rate for substantial O_3/O_x production. The main basis of this conclusion is that in ordinary urban atmospheres, Cl atoms are effectively scavenged by the unavoidably present hydrocarbon pollutants. In rural atmospheres, it is additionally the extremely low concentrations at which PCE typically occurs. Thus contrary to the smog chamber data and to the viewpoint held thus far within EPA, PCE is now judged to contribute less to the ambient photochemical O_3/O_x problem than equal concentrations of ethane.

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